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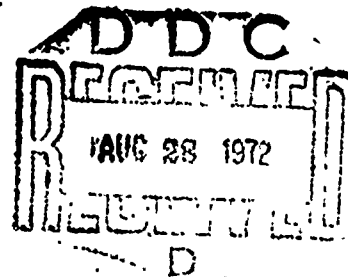
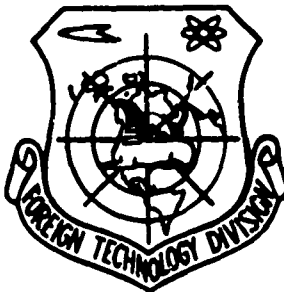
FOREIGN TECHNOLOGY DIVISION



SOME REGULARITIES IN THE PRECIPITATION OF MOLYBDENUM
ORIENTED COATINGS FROM GASEOUS PHASE

by

A. I. Yevstyukhin, D. D. Abanin, et al.



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13. ABSTRACT <p>The paper describes an experiment in precipitation of molybdenum from gaseous phase in an attempt to determine the factors which affect the orientation of precipitation coatings. In this experiment, high-temperature pyrolysis of molybdenum pentochloride was used. Application of the coating was accomplished at three fixed temperatures of the base: 1120, 1300, and 1430°C. Two types of bases were used: rolled molybdenum, foil and tablets. X-ray analysis of the coatings was performed. Change in the temperature of the base and change in pressure of the gaseous phase were found to affect the coating process. Texture of the base was found not to have a dominant effect on texture of the coating. The texture of the coatings obtained was formed by a series of orientations: [111]-[112]-[013]-[001].</p> <p>Details of illustrations in this document are better shown on microfiche</p>			

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А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

SOME REGULARITIES IN THE PRECIPITATION OF MOLYBDENUM ORIENTED COATINGS FROM GASEOUS PHASE

A. I. Yevstyukhin, D. D. Abanin,
V. I. Mel'nikov, and Yu. A. Perlovich

INTRODUCTION

The problem of obtaining crystallographically uniform metallic surfaces, repeatedly discussed in literature [1-5] over the last decades and until recently a matter of interest predominantly from the point of view of the general theory of crystallization, today has acquired an important significance in connection with the necessity which has arisen for perfecting thermionic converters.

In published works on the obtaining of oriented coatings from refractory metals mainly various precipitation methods from gaseous phase were used. Thus, in [1] and [2] for precipitation of molybdenum and tungsten a method of thermal dissociation of the carbonyls of these metals in the presence of hydrogen is used; in [3] and [4] for the same purposes the reduction of hexafluoride by hydrogen was conducted; in [5] both the reduction of molybdenum hexafluoride by hydrogen and high-temperature pyrolysis of molybdenum pentachloride was used. In some of the works mentioned, the authors connect the observed changes in the preferred crystallographic orientation of the coating with the change

in such parameters of the process as the temperature of the base [2] or the ratio of the partial pressure of the components of the gas mixture [4].

For the precipitation of molybdenum coating we used a high-temperature pyrolysis of molybdenum pentachloride. The qualitative dependence of the character of the preferred orientations registered by X-ray diffractometric research on the coatings on the totality of the parameters of the process of application of the coating was established.

EQUIPMENT AND METHOD OF COATING

The coating process was conducted in a reaction flask made of molybdenum glass evacuated to a pressure of $5 \cdot 10^{-6}$ mm Hg and sealed from the vacuum system with hermetically sealed welded molybdenum leads. Pentachloride was distilled into a special extension of the reaction flask after which it was placed in the heating system which consists of two independent furnaces. A more detailed account of the procedure of preparation of the flask for the process is described in [6]. In all the experiments in precipitation the temperature of the flask was kept constant and equal to $400 \pm 20^\circ\text{C}$. The pressure of pentachloride in the system was determined by the temperature of the extension which was controlled with the aid of a self-balancing potentiometer to within $\pm 2^\circ\text{C}$. The temperature of the base was changed within a range of $1100\text{--}1450^\circ\text{C}$ and was measured by an optical pyrometer.

As the basis for the process lies the transfer of molybdenum from the initial metal to the precipitation surface according to the reversible reaction



The calculation dependence of the degree of dissociation of molybdenum pentachloride on temperature for the fixed pressures

P_1 and P_2 ($P_2 > P_1$) is given in Fig. 1. The working temperature range of the base is limited on one hand by the insignificant rate of increase in precipitate with the small degree of dissociation of the molecules of pentachloride and, on the other hand, by the impossibility of obtaining high temperatures when using glass reaction flasks.

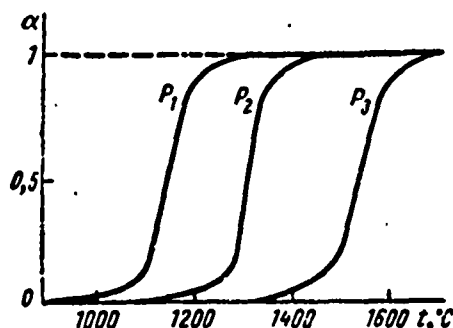


Fig. 1. Calculation dependences of degree of dissociation of molybdenum pentachloride on temperature for fixed pressures ($P_1 = 10^{-4}$ atm, $P_2 = 10^{-3}$ atm, $P_3 = 10^{-2}$ atm).

Apart from the reaction of the dissociation of pentachloride to the increase of coating, a great effect is rendered by the process of removal of molybdenum from the base as a result of the interaction of higher chlorides with molybdenum according to reactions of the type



The joint progress of all the indicated reactions whose rates depend differently upon temperature and pressure causes the existence of the areas of precipitation and corrosion divided by the "zero increase" curve or, according to Schaeffer [7], the critical curve of decomposition. The "zero increase" curve is depicted in Fig. 2.

Application of coating was accomplished at three fixed temperatures of the base: 1120, 1300, and 1430°C and temperatures of the extension from 78 to 140°C corresponding to the pressure range of pentachloride of 0.04 to 3 mm Hg.

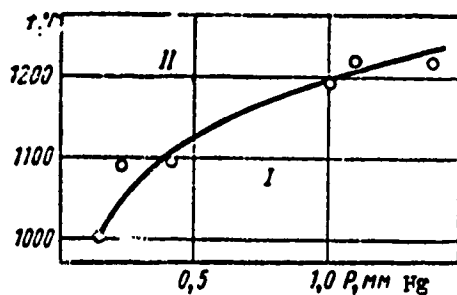


Fig. 2. Change in the "zero increase" curve depending on the pressure of chlorine and temperature of the sample: I - area of corrosion; II - area of precipitation.

In applying the coating two types of bases were used: rolled molybdenum foil with a thickness of 0.3 mm and tablets with a thickness of 2 mm prepared by the cermet method at a sintering temperature of 1700°C. Samples for precipitation had the form of disks 20 mm in diameter. The disks cut from foil were pre-annealed in a vacuum at a temperature of 1400°C for 1 h in order to avoid the effects of recrystallization on the structure of the precipitate in the course of precipitation. In parallel with the recrystallization of the base there occurred vacuum cleaning of the surface.

X-RAY ANALYSIS OF COATINGS

Quantitative X-ray analysis of the preferred orientation of coatings was conducted on a URS-50IM diffractometer on CuK_α emission. A diagram of the photographing and the principles of the processing of results are similar to those utilized in the method of reverse pole figures [8, 9]. The degree of participation of p of one or another crystallographic plane (hkl) in forming the plane of the surface of the obtained sample were estimated on the strength of the relation

$$\rho(hkl) = \frac{I(hkl)}{\sum I(hkl)} \frac{\sum I'(hkl)}{I'(hkl)},$$

where $I(hkl)$ - the intensity of the X-ray diffraction line (hkl) of the sample being investigated, $\sum I(hkl)$ - the sum of the intensities of all the recorded lines of the sample; $I'(hkl)$ and $\sum I'(hkl)$ - the intensity of the corresponding line and the sum of intensities for a textureless standard.

As a standard a layer of pressed molybdenum powder was used. In this case, if $p(hkl) < 1$, then a relatively smaller part of grains than in the textureless standard is oriented in such a way that plane (hkl) is parallel to the surface. And vice versa, when $p(hkl) > 1$ preferred orientation takes place.

In order to explain the effect of the base on the orientation of the precipitate, we investigated the form and extent of textural maximums for certain planes within the limits of the space angle, the central axis of which coincides with the normal to the surface both for the obtained coating and the for initial base. Photographing of texture was conducted according to the usual procedure or diffractometric determination of texture on reflection [9]. For this purpose a GP-4 goniometric attachment was used, making it possible to bring into reflecting position the planes, the normals to which are located within the limits of the space angle which is interesting to us.

Parameters of the process of precipitation and orientation of coatings

(1) Номер с. д. н. а.	(2) Температура осн. °C	(3) Температура растяж. °C	(4) Скорость осаждения, мкм/мин	(5) Толщина покрытия, мкм	$p(hkl)$					
					(001)	(011)	(111)	(112)	(013)	(123)
1	1120	78	0.1	50	—	0.2	11.4	1.2	1.1	1.0
2	1120	105	0.2	60	—	0.1	13.8	1.7	0.8	1.1
3	1300	78	0.1	20	0.1	0.1	5.5	3.4	0.4	1.1
4	1300	98	2.5	100	0.2	0.3	0.6	1.5	6.1	0.6
5	1300	116	2.2	60	7.5	0.2	—	0.6	1.6	—
6	1300	125	1.7	150	10.8	0.1	—	0.1	0.2	—
7	1300	130	1.0	20	10.9	—	0.8	—	0.0	—
8	1430	80	0.7	130	—	—	35.5	—	—	—
9*	1430	100	1.0	60	0.1	0.1	19.2	0.1	—	1.0
10*	1430	116	1.7	100	0.3	0.3	14.6	1.2	0.1	0.7
11	1430	125	2	50	7.2	0.1	1.4	0.4	2.0	0.2
12	1430	130	2.2	40	11.2	—	1.0	0.1	—	—
(6) Фольга	—	—	—	—	10.1	0.1	1.6	0.2	0.2	0.1
(7) Таблетка	—	—	—	—	1.2	0.9	1.2	1.0	1.3	1.0

* Coating applied to table.

KEY: (1) Sample number; (2) Temperature of base, °C; (3) Temperature of extension, °C; (4) Rate of precipitation, $\mu\text{m}/\text{min}$; (5) Thickness of coating, μm ; (6) Foil; (7) Tablet.

Data on the processes of precipitation and the results of X-ray analysis of the samples are provided in the table. Errors in determining $p(hkl)$ for different (hkl) are different and they depend, furthermore, upon the contribution of preferred orientation.

METALLOGRAPHIC RESEARCH ON COATINGS

By comparing the surfaces of the obtained coatings, it is possible to note the dependence of the morphology of surface on the rate of precipitation. As the conditions of precipitation change, there are clearly traced the same stages in growth of coatings which were also noted in [2]; namely: a stage which is characterized as relatively smooth, formed by finely dispersed surface irregularities (Fig. 3a); a stage of appearance of drop-like formations lacking faceting (Fig. 3b) which arose as the result of the intensive process of homogeneous separation of metal in the space adjacent to the base, leading to very considerable supersaturation; a stage which is characterized by the formation of considerable micro-roughness with crystal faceting (Fig. 3c) and corresponding to the inversion of the mechanism of condensation from the system vapor-liquid-crystal to the system vapor-crystal.

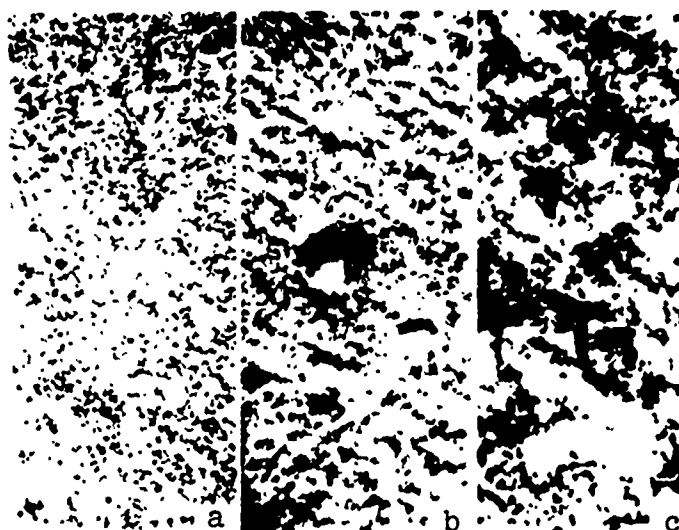


Fig. 3. The surface of the coatings obtained ($\times 120$); (a) Sample No. 2; (b) Sample No. 4; (c) Sample No. 5.

However, it should be noted that in the case in question the transition from one stage in the growth of coating to another was observed not only with a change in temperature of the base, as in [2], but also with a change in pressure of the gaseous phase.

Furthermore, comparison of the morphology of the surface and diffractometric data concerning the orientation of coatings applied at 1120 and 1300°C indicates that the tendency described above of the change in morphology of the surface accompanies a tendency to replacement of the preferred orientation of the type [111] by the preferred orientation of the type [001] as was noted in [2] for the carbonyl process. However the data obtained for the coatings precipitated at 1430°C do not make it possible to explain the character of the morphology of surface by the type of detectable preferred orientation.

The microstructures of cross sections of the coatings are more or less uniform (Fig. 4). Some distinctions are observed in a comparison of the cross sections corresponding to the sections of the sample in parallel and perpendicular to the direction of rolling of the foil-base.



Fig. 4. Microstructure of a cross section of coating ($\times 120$).

DISCUSSION OF RESULTS

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The data obtained as a result of quantitative diffractometric research on the preferred orientation of coatings make it possible to reveal a number of regularities in the process of texture-formation in the precipitated layers.

As can be seen from the table, orientations [111], [013], and [001] were obtained in the purest form. All other variants are intermediates — they form a continuous transition from orientation [111] to orientation [001]. In this case, having arranged the data on orientation of the bases of coatings applied at a determined temperature in ascending order of increase in the pressures of the gaseous phase, there is detectable for all six recorded crystallographic planes a regular character of continuous change in their contribution to axial texture.

Due to the negligibly small rate of precipitation it was impossible to apply a coating at 1120°C and the pressure which corresponds to the temperature of the extension (above 105°C).

The general curves of dependence of the rate of growth of coating on the pressure of the gaseous phase (Fig. 5) for the determined temperature possess a clearly expressed maximum which increases and shifts somewhat in the direction of higher pressures with the increase in temperature of the base [10]. Moreover, the left drop in the curve is caused, apparently, by a deficiency in molecules — the carriers of molybdenum at reduced pressures, while the right drop is connected with the approach to the critical of the curve of decomposition. For the processes conducted at 1300°C, the maximum of the rate of growth was in the interval of the utilized pressures, but at 1430° within the limits of the indicated range there was room for only the left branch of the curve.

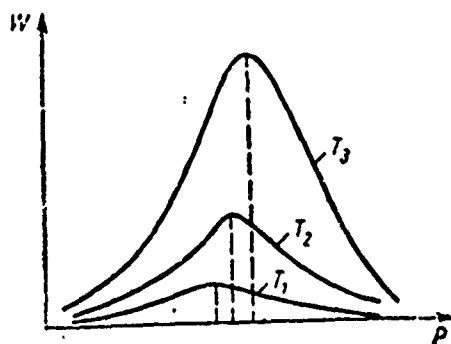


Fig. 5. Dependence of the rate of growth of coating W on the pressure of gaseous phase P at various temperatures of base T ($T_1 < T_2 < T_3$).

With an increase in the temperature of the base simultaneously with the rate of growth a shift in the direction of the higher pressures is suffered by the curves of dependence of $p(hkl)$ on the temperature of the extension (Fig. 6) which can be constructed from the data contained in the table. Thus the table shows that with an increase in temperature of the base from 1300 to 1430°C the maximum for orientation [112] and the beginning of a sharp increase in the intensity of orientation [001] are displaced towards the pressures corresponding to high temperatures of the extension.

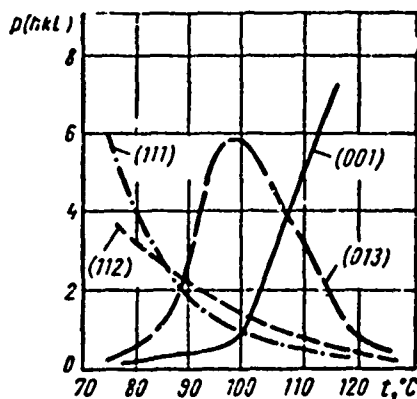


Fig. 6. Curves of dependence of $p(hkl)$ on temperature of the extension.

However, as far as it is possible to judge by the results obtained, the dependence of the orientation of the coating on the temperature of the base only as a first approximation can be reduced to a simple shift in the direction of high pressures. At the same time, the deviations from this dependence which are developed during comparison of the results of research on coatings applied at 1300 and 1430°C can be explained by the small number of conditions of precipitation which were used. As a result, the quantity of data given in the table proves to be insufficient for reproduction of the complete form of dependence.

In reference works [3-5] there is a report on obtaining only orientations [001] and [111]. Despite the sharp differences in the temperatures of precipitation issuing from the distinction in

procedures (in the reduction of hexafluoride by hydrogen the temperature of the base is changed in the range of 600-800°C), the results prove to be partially similar. This fact, and also the above-noted shift in the distribution of grains on orientations in the direction of high pressures observed during the temperature increase of the base in our experiment, make it possible to assume that in the precipitation of molybdenum from gaseous phase in a sufficiently wide temperature range the orientation of the precipitate is determined not by the individual externally controllable parameters but by the intensity of the liberation of the precipitating metal as a result of the reactions taking place. Thus, the authors of [4] established the dependence of the orientation of the coating on the molar ratio being contained in gaseous phase of H_2 and WF_6 which in a wide range of temperature and pressures controls the output of the metal. Analogically, the continuous series of orientations observed in our experiment indicates the dependence of the obtained orientation of the coating on the rate of precipitation of the metal.

The textural maximums of coating possess cylindrical symmetry, i.e., in a plane the surfaces of the coating of the direction of preferred orientation are absent. But textural maximums of recrystallized foil-bases, for example, for plane (001) possess a total of two planes of symmetry whereby the form of these maximums in sections is considerably more complex than the form of the maximums (001) of a coating determined in section by gaussian distribution. The sintered tablet of molybdenum used as a base for the three samples does not possess any texture.

Thus, the absence of conformity in form and extent of textural maximums can serve as evidence of the absence of the effect of the orientation of the base on the orientation of a heavy coating. At the same time, the comparatively slight change in condition during the transition from precipitation on the sintered tablet (see table, sample No. 10) to precipitation on foil (sample No. 11) gives rise to a sharp increase $p(001)$ and

a decrease in $p(111)$. These abrupt changes, although they correspond to the general change in axial texture, apparently, have been conditioned by preponderance in the foil of the base of grains in which the normal to the plane (001) coincides with the normal to the surface. On the basis of the findings it is possible to confirm that the effect of the orientation of the base on the orientation of the coating is not the dominant factor.

Further, the character of the change in distribution of grains in respect to orientations makes it possible to establish that in proportion to the decrease in the degree of inequilibrium of the process the normal to the plane of the surface of the coating is shifted within the limits of an elementary stereographic triangle from $[111]$ to $[001]$ in the direction $[111]$ - $[112]$ - $[013]$ - $[001]$ (Fig. 7). On samples No. 3-7 and 8-12 the various stages of this transition show up well if we remember that the position of the normal in the stereographic triangle corresponds only to the most probable orientation. Curves in Fig. 6 constructed according to the tables do not reflect all the details of the process of transition. Thus, if we accidentally succeeded in selecting the condition of precipitation in such a way that the intermediate preferred orientation $[013]$ appeared, then one should expect that during the conducting of the process at 1300°C and a temperature of the extension of $80-100^{\circ}\text{C}$ the coating will possess preferred orientation $[112]$.

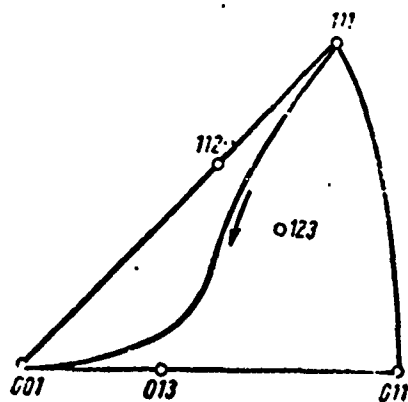


Fig. 7. Change in orientation of coating with increase in pressure (movement from $[111]$ to $[001]$).

The noted regularity of the change in orientation of the coating precipitating from the gaseous phase differs from the regularity for the precipitate of metal from a body-centered cubic lattice obtained from melt [11] where the observed orientation is connected with supersaturation and the normal to the surface of coating is transferred within the limits of a single stereographic triangle on two closed branches beginning in [011]. Such a distinction, apparently, is completely natural because the process of texture formation being determined by the relationship of the rates of normal and tangential growth should substantially depend upon the nature of the adjoining phases.

CONCLUSIONS

1. By the method of high-temperature pyrolysis of molybdenum pentachloride there have been obtained molybdenum coatings whose texture has been formed by a continuous series of orientations [111]-[112]-[013]-[001] which are respectively changed in proportion to the decrease in the degree of inequilibrium of the process of precipitation.

2. Comparison of the form and extent of the textural maximums of the base and coatings indicates the absence of a predominant effect of the texture of the base on the orientation of the coating.

3. On the basis of literature and our experimental data concerning the morphology of the surface and the orientation of the coatings, there has been established the identity of the regularities of forming of coatings using various methods of precipitation from the gaseous phase.

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